

PATENT SPECIFICATION

(11) 1 458 570

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- (21) Application No. 50923/74 (22) Filed 25 Nov. 1974
- (31) Convention Application No. 420 728
- (32) Filed 30 Nov. 1973 in
- (33) United States of America (US)
- (44) Complete Specification published 15 Dec. 1976
- (51) INT CL² C07C 43/04; C07D 321/12, 323/00//C07C 69/22
- (52) Index at acceptance
 C2C 178X 20Y 215 231 240 247 253 25Y 263 26X 305
 30Y 360 361 362 364 366 368 36Y 37X 382 491
 497 500 50Y 606 607 623 624 628 633 634 638
 643 644 648 658 672 67X 774 796 79Y BJ CV
 WJ YB

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(54) PROCESS FOR PREPARING POLYGLYCEROL

(71) We, THE PROCTER & GAMBLE COMPANY, a Corporation organised and existing under the laws of the State of Ohio, United States of America, of 301 East Sixth Street, Cincinnati, Ohio 45202, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in an by the following statement:—

This invention relates to a process for preparing polyglycerol, and more particularly to a process for preparing polyglycerol by heating glycerol under reduced pressure in the presence of a catalytic amount of adjuvant system capable of promoting the polymerization reaction. The adjuvant system comprises sulphuric acid and a lower aliphatic acid ester of glycerol. When from 25% to 75% of the glycerol is polymerized, the glycerol polymerization is terminated by inactivation of the adjuvant system. This is done by neutralizing the adjuvants with a substantially stoichiometric amount of a neutralizing agent. At least part of the unreacted glycerol and cyclic diglycerol are then removed by distillation. The polglycerol mixture so prepared contains a high percentage of linear di- and triglycerols and a low percentage of polyglycerols comprising seven or more glycerol units. The polyglycerol mixture can be esterified with a fatty acid in known manner to provide polyglycerol fatty acid esters having a polglycerol distribution which is substantially similar to that of the polyglycerol prior to esterification. These esters are particularly suitable for use as emulsifiers in food applications.

Polyglycerols and the corresponding esters of these polyglycerols and higher fatty acids are known food additives, especially emulsifiers, and also have been used for various food applications. For example, polyglycerol fatty acid esters have been used as anti-

45 spattering agents in cooking and salad oils as disclosed in U.S. Patents 3,415,658 and 3,415,659. U.S. Patent 3,528,832 relates to a fluid shortening containing a polyglycerol fatty acid ester emulsifier.

50 It is known that polyglycerol fatty acid esters can be prepared by polymerizing glycerol in the presence of an alkaline or acid condensation catalyst. The esterification of the polyglycerols so prepared with fatty acids in the presence of an esterification catalyst is also known. The catalytic polymerization of glycerol to polyglycerol is, for instance, described in U.S. Patent 2,487,208. The polymerization is carried out under atmospheric pressure at an elevated temperature, for example, from 55 200°C to 280°C. Alkali metal and alkaline earth metal compound condensation catalysts can be used. Canadian patent 834,214 discloses the preparation of monoesters of polyglycerol and fatty acids whereby the alkaline condensation catalyst employed is not merely deactivated, but is essentially completely removed from the condensation reaction mixture prior to esterification. For that purpose, the condensation reaction mixture is contacted with both anionic and cationic exchange resins.

60 U.S. Patent 2,182,397 relates to a process for forming ether derivatives of polyhydric alcohols including derivatives that contain esterified fatty acid groups. The polyhydric alcohol, e.g. glycerol, is partially esterified with a carboxylic acid containing two or more carbon atoms. The etherification (polymerization) is carried out in the presence of a water carrier and an esterifying catalyst such as sulfuric acid and certain aromatic sulfonic acids. It is also mentioned that the acid catalyst can be neutralized.

65 70 75 80 85 While the art is crowded and diverse, it fails to recognize that polyglycerol mixtures having a particular distribution of highly



- functional emulsifier precursors can be prepared by polymerization of glycerol in the presence of adjuvants capable of controlling the polymerization reaction. It has been disclosed that the neutralization of an alkaline condensation catalyst is deficient as presumably traces of the alkaline material escape neutralization and accordingly are present during the subsequent esterification reaction.
- The contained polymerization of glycerol and lower polyglycerols to higher polyglycerols is thereby promoted. It is observed that in polymerizing glycerol in the presence of an alkaline catalyst, acid by-products are formed.
- During the condensation process these by-products react with the alkaline catalyst to form organic salts which cannot be easily deactivated or removed and which act as condensation and interesterification catalysts.
- More specifically in accordance with this invention we provide a process for preparing polyglycerol comprising:
- heating glycerol to a temperature in the range from 110—180°C. at an absolute pressure below 400 mm of mercury in the presence of from 0.03 to 3% by weight of sulphuric acid, based on the weight of the glycerol, and from 0.1 to 10% by weight, based on the weight of the glycerol, of a glyceride compound of the formula (I):
- $$(R_1COO)_nC_3H_5(OH)_{3-n} \quad (I)$$
- where R₁ is CH₃— or CH₃.CH₂—, and n is an integer from 1 to 3, the groups R₁ being identical or different when n is 2 to 3, until from 25% to 75% of the glycerol is polymerized;
- inactivating said sulphuric acid by the addition of a substantially stoichiometric amount of neutralizing agent; and
 - removing at least part of the unreacted glycerol by distillation.
- The polyglycerol so prepared can be esterified with a fatty acid to provide a polyglycerol fatty acid ester which can advantageously be used as an emulsifier ingredient in food applications.
- In the first step of the process of the invention glycerol is heated to a temperature from 110° to 180°C, preferably from 120°C to 145°C, under an absolute pressure below 400 m.H., preferably from 1 mm to 20 mm absolute mercury pressure. The glycerol condensation is carried out in the presence of an adjuvant system comprising from 0.03% to 3% by weight, preferably from 0.08% to 0.3% by weight of sulfuric acid based on the weight of the glycerol; and from 0.1% to 10% by weight, preferably from 0.5% to 5% by weight, based on the weight of the glycerol, of a glyceride having the formula (I). The polymerization is conducted until from 25% to 75%, preferably from 35% to 60%, of the glycerol is polymerized.
- The condensation (polymerization) temperature is in the range of from 110° to 180°C. Heating the reaction mixture to a temperature below 110°C results in some glycerol polymerization; however, the reaction speed is insufficient to be of practical interest. Carrying out the condensation reaction at a temperature above about 180°C can result in the formation of a polyglycerol having an undesirable color and odor.
- The condensation reaction is carried out under a pressure below 400 mm absolute mercury pressure. Glycerol polymerization at a higher pressure tends to be too slow.
- The adjuvant system comprises sulfuric acid and a lower carboxylic acid ester of glycerol. The latter is represented by the esterification product of glycerol with acetic or propionic acid. Mixed esters can also be used. Highly preferred for use herein are mono-, di-, and tri-acetin. It will be appreciated that the glyceride can also be prepared in situ from its precursors, i.e. acetic or propionic anhydride and glycerol.
- The glycerol condensation is catalyzed by the addition of sulfuric acid and a particular glycerol ester in the quantities defined hereabove. The minimum amounts of sulfuric acid (0.03%) and glyceride (0.1%) are needed to noticeably perceive the advantages of the claimed process. Using more than 3% of sulfuric acid can contribute, particularly towards the end of the condensation reaction, to charring of organic material and to the inherent formation of undesirable by-products. Using more than 10% of the glyceride can, as a result of interesterification, contribute to the formation of low molecular weight carboxylic acid esters of polyglycerol. These latter compounds can adversely affect the emulsifying properties of the polyglycerol fatty acid esters.
- The glycerol condensation is terminated when from 25% to 75%, preferably from 35% to 60%, of the glycerol is polymerized. The endpoint of the condensation may be determined by means of refractometer index readings (Butyro scale at 60°C) as described in "OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS", ninth edition, 1960; published by Association of Official Agricultural Chemists, Washington, D.C., page 359. Apparently, in the glycerol polymerization process the initial rate of diglycerol formation is higher than that of the longer chain polymers. The diglycerol content reaches its maximum concentration when about 50% of the glycerol has been polymerized. From that point onwards, the rate of diglycerol formation is lower than

the rate at which diglycerol is further polymerized. Accordingly, the concentration of diglycerol decreases. Thus, a high polymerization completeness corresponds to a broad 5 polymer species distribution. This, in turn, is useful as the concentration of the lower polyglycerol can, to a certain extent, be varied by terminating the condensation reaction at more or less advanced level of glycerol 10 densification within the claimed range.

During the condensation, gas, preferably nitrogen, sparging and/or mechanical agitation is normally applied.

As used in the specification and claims 15 herein, the terms "polyglycerol" and "poly-glycerol mixture" are employed interchangeably and refer not only to pure polyglycerol and mixtures thereof, but also to a mixture of compounds which comprises a mixture of glycerol, diglycerol and homologous poly-glycerol molecules. The terms (glycerol) "polymerization" and "condensation" are used interchangeably to define the reaction resulting in the etherification of two or more molecules 25 of glycerol with formation of water. The terms "adjuvants(s)", "adjuvant system" and "catalyst" are also used interchangeably to define the function of the combination of the sulphuric acid and the glycerol derivative 30 as being to modify or increase the rate of glycerol polymerization in a catalytic manner, i.e., without undergoing substantial chemical changes during the condensation reaction.

When the desired degree of glycerol 35 densification is attained, the polymerization is terminated by neutralizing the catalyst, i.e. essentially the sulphuric acid, with a substantially stoichiometric amount of a suitable neutralizing agent. Any suitable neutralizing 40 agents may be used, including, by way of example, alkali metal and alkaline earth metal hydroxides, carbonates, and bicarbonates such as sodium hydroxide, potassium hydroxide, lithium hydroxide, barium hydroxide, calcium 45 hydroxide, sodium carbonate, sodium bicarbonate and potassium bicarbonate, and calcium oxide. This enumeration is not intended to be limiting as other 50 neutralizing agents can be employed. It may be desirable to cool the reaction mixture during neutralization, particularly when the level of sulphuric acid present is above about 1%. This eliminates the danger of overheating which can cause deterioration of the 55 reaction mixture (color and odor).

Following the inactivation (neutralization 60 of the catalyst, at least part of the unreacted glycerol and preferably also the largest part of the cyclic diglycerol are distilled off. This is normally done at a temperature in the range from 150° to 300°C at a pressure below 400 mm, preferably in the range from 1 to 20 mm absolute mercury pressure. This set of distillation conditions represents a

practical optimization for the purpose of removing the undesired glycerol without adversely affecting the overall quality, particularly color and odor, and emulsifying properties of, for example, the polyglycerol fatty acid ester prepared from the polyglycerol made by the claimed process.

It will be appreciated that the polyglycerol distribution of the corresponding polyglycerol fatty acid esters is critical to the attainment of superior emulsifying properties in food applications. Polyglycerol esters known in the art and containing less than 25% by weight of the di- and triglycerol esters are unsatisfactory from the standpoint of providing acceptable emulsifying properties to shortenings. Similarly, polyglycerol esters containing high levels, e.g. more than 15%, by weight, of mono- and diglycerides (mono- and diesters of glycerol) or long-chain (more than 7 glycerol units) polyglycerol esters are not suitable for producing superior food applications. The presence of mono- and diglycerides is detrimental to the performance of poly-glycerol esters in most food applications. While the detrimental effect of the β-tending di-glycerides is instantaneous, the effect of mono-glycerides is slower and shows up more gradually upon ageing. Mono- and diglycerides can be present in polyglycerol esters as a result of contamination. Thus, the polymerization completeness of glycerol to poly-glycerol will affect the amount of glycerine present in the polyglycerol and available for the formation of mono- and diglycerides in a subsequent esterification reaction. As pointed out before, a complete conversion of glycerol to polyglycerol will provide high levels of long-chain polyglycerols such as hexa- hepta, and octaglycerols. However, these long-chain polyglycerols yield monoesters which are neither fat-soluble nor functional emulsifiers. In view of the unsatisfactory emulsifying properties of polyglycerol esters containing mono- and diglycerides, esters of so-called "average" hexa and higher polyglycerols have been preferred for food applications because they contain only minor amounts of mono- and diglycerides. After at least part of the unreacted glycerol and of the cyclic diglycerol have been removed, the remaining poly-glycerol mixture contains a high level of lower (di and tri-) polyglycerols and a low level of polyglycerols containing 7 or more glycerol units. The polyglycerol can then be esterified with a fatty acid or a mixture of fatty acids to provide food emulsifiers and their use in food technology is described in our British Patent Applications:

1. Liquid Pumpable Shortening, inventors Paul Seiden and John R. Shaffer, Application No. 50921/74 (Serial No. 1458568) and
2. All Purpose Liquid Shortening Com-

positions, inventor Paul Seiden, Application No. 50922/74 (Serial No. 1458569).

- 5 It can be desirable to additionally tailor the polyglycerol composition described hereinbefore. The term "tailor" is meant to express that the length of the polyglycerol chain, which is used for preparing the corresponding emulsifier ester, can be varied for specific 10 (tailor-made) applications. For example, the above polyglycerol composition prepared by the process of this invention can be distilled from about 235° to about 255°C at 5 mm absolute mercury pressure to fractionate the linear glycerol in combination with a minor amount of glycerol. The latter is then removed in a separate distillation step.

20 The polyglycerol compositions herein can be esterified or interesterified with fatty acid to provide highly functional polyglycerol ester emulsifiers. When the polyglycerol is to be used, after esterification, as a food emulsifier, it is desirable that the polyglycerol ester be substantially free of odor and also have a 25 bland taste. For that purpose, the polyglycerol ester is preferably deodorized. Composition alterations can occur, which frequently can lead to a loss of functionality, if the deodor-

ization is carried out on polyglycerol ester alone or in combination with a shortening. These alterations can be conveniently avoided by carrying out the deodorization process in the presence of an excess of polyglycerol, preferably immediately after the esterification reaction is completed. The deodorization is preferably carried out at the same temperature as the esterification reaction.

30 35 The following examples demonstrate the invention and facilitate its understanding.

Example I.

40 Four hundred sixty six pounds glycerol, 11.95 pounds technical grade monoacetic and 239 grams sulfuric acid were charged to a stainless steel reactor equipped with a nitrogen sparging ring and mechanical agitation. The glycerol polymerization was carried out at 132°C and 5 mm absolute mercury pressure. The polymerization reaction was terminated through the addition of 180 grams sodium hydroxide when the refractive index reached 72.7 (at 60°C on the Butyro scale). At this stage 54.8% of the glycerol was polymerized. The composition of the reaction mixture and the refractive index had evolved as can be seen from the following Table:

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Refractive Index (Butyro Scale: 60°C)		66.6	70.1	71.0	72.7
Glycerol	%	58.9	52.4	48.2	45.2
Linear diglycerol	%	24.4	27.7	28.7	29.1
Cyclic diglycerol	%	1.7	1.7	1.8	2.5
Linear triglycerol	%	8.8	10.4	11.0	12.0
Cyclic triglycerol	%	1.2	1.2	1.4	1.6
Linear tetraglycerol	%	3.2	4.0	5.6	6.0
Linear pentaglycerol	%	1.2	1.6	2.1	2.2
Hexaglycerol	%	0.6	1.0	1.2	1.4

60 Glycerol and cyclic diglycerol were then distilled off at temperatures from 150°C to 205°C and 5 mm absolute mercury pressure. The distillation was monitored by refractive

index control. When the refractive index attained 87.5 the distillation was completed. The polyglycerol so produced had the following composition:

Component	Polyglycerol Compositions in % By Weight
Glycerol	2.3
Linear diglycerol	55.2
Cyclic diglycerol	0.5
Linear triglycerol	22.1
Cyclic triglycerol	1.4
Linear tetraglycerol	9.2
Cyclic tetraglycerol	1.2
Linear pentaglycerol	5.2
Hexaglycerol	1.8
Heptaglycerol	0.6
Glycerol of more than seven glycerol units; organic and inorganic salts; polymerization by-products; moisture	
— Balance to 100 —	

5 Eighty pounds of the above polyglycerol composition were esterified in a known manner with 55 pounds of food grade stearic acid. The polyglycerol fatty ester obtained exhibited outstanding emulsifying properties when used in cakes and fluid shortenings.

10 Example II.
The polyglycerol composition of Example I was additionally tailored. 165 pounds of that particular polyglycerol were charged to a stainless steel reactor equipped with a nitrogen sparging ring, steam and electrical heating devices, mechanical agitation, con-

densers, receivers and vacuum outlets. The polyglycerol was gradually heated from 243°C to 268°C under 5 mm absolute mercury pressure whereby the linear diglycerol and the remaining glycerol were distilled off. The operation was discontinued when 83 pounds were collected. To remove the minor amount of glycerol from the distillate, the latter was recharged to the stainless steel reactor and maintained at about 227°C under 5 mm absolute mercury pressure for about one hour. The remaining mainly linear diglycerol had the following composition:

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Component	Polyglycerol Compositions in % By Weight
Glycerol	trace
Linear diglycerol	85.1
Cyclic diglycerol	0.2
Linear triglycerol	6.6
Cyclic triglycerol	2.3
Linear tetraglycerol	4.5
Cyclic tetraglycerol	0.1
Linear pentaglycerol	0.6
Glycerol of more than seven glycerol units; organic and inorganic salts; polymerization by-products; moisture	
	Balance to 100

5 Thirty-five pounds of this polyglycerol were added to a stainless steel reactor equipped with mechanical agitating device, electric heating device, and nitrogen spargin, 23.3 pounds of food-grade stearic acid were added, whereafter, the reaction was heated under agitation to a temperature of about 238°C. The esterification was carried out under a 10 pressure of about 11 inches mercury. When the free fatty acid content dropped below 2% by weight, the esterification product was deodorized under an absolute pressure of 6 millimetre mercury for about one hour under agitation and nitrogen sparging. The 15 reaction product contained 0.1% by weight free fatty acid and was a polyglycerol fatty acid emulsifier useful for a wide range of food applications inclusive of cake baking, pie crust, salad dressing and frying. Thirty-five percent of the hydroxyl groups of the polyglycerol were reacted.

WHAT WE CLAIM IS:—

- 25 1. A process for preparing polyglycerol comprising:
 (a) heating glycerol to a temperature in the range from 110—180°C. at an absolute pressure below 400 mm of mercury in the presence of from 0.03 to 3% by weight of sulphuric acid, based on the weight of the glycerol, and from 0.1 to 10% by weight, based on the weight of the glycerol, of a glyceride compound of the formula:



where R_1 is CH_3- or $CH_3\cdot CH_2-$, and n is an integer from 1 to 3, the groups R_1 being identical or different when n is 2 or 3, until from 25% to 75% of glycerol is polymerized;

35 (b) inactivating said sulphuric acid by the addition of a substantially stoichiometric amount of neutralizing agent; and

40 (c) removing at least part of the unreacted glycerol by distillation.

45 2. A process according to claim 1 in which the glycerol is heated to a temperature in the range from 120 to 145°C. at an absolute pressure from 1 to 20 mm of mercury.

50 3. A process according to claim 1 or claim 2 in which the proportion of sulphuric acid is from 0.08 to 0.3% by weight of the glycerol and the proportion of glyceride compound is from 0.5 to 5% by weight of the glycerol.

55 4. A process according to any of the preceding claims in which the glyceride compound is mono-, di or triacetin.

60 5. A process according to any of the preceding claims in which the reaction is terminated when from 35 to 60% of the glycerol is polymerized.

65 6. A process according to any of the preceding claims in which the neutralizing agent is an alkali metal or alkaline earth metal hydroxide, carbonate or bicarbonate.

7. A process for preparing polyglycerol substantially as herein described in Example I.

8. Polyglycerol whenever produced by a process according to any one of the preceding claims.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1976.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.